Chain Stopper-Assisted Characterization of Supramolecular Polymers

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ABSTRACT: Supramolecular polymers are dynamic materials; consequently, their molar mass is concentration dependent. However, the present experimental results show that an efficient chain stopper (i.e., a monofunctional monomer) can be used to block the concentration dependence of the molar mass of a hydrogen-bonded supramolecular polymer, over a realistic concentration range. This fact was used to derive the molecular weight and radius of gyration of the stopped supramolecular chains (by light scattering) as well as the intrinsic viscosity. In a second step, the molecular weight of the bis-urea-based supramolecular polymer (EHUT) was determined in the absence of a chain stopper.

Introduction

Supramolecular polymers are chains of small molecules held together through reversible noncovalent interactions.[1−3] This reversibility is desirable because it is responsible for the appearance of new properties as compared to those of usual covalent polymers. For instance, improved processability can be expected from the temperature dependence of the molar mass of supramolecular polymers.[4] Moreover, self-healing materials[5,6] may be obtained because of the dynamic nature of the chains.

However, this reversibility is also a drawback as far as characterization is concerned. In particular, molar mass measurement is impeded by the fact that molar mass changes with concentration. Thus, classical polymer characterization techniques such as size exclusion chromatography, static light scattering, or osmometry cannot be used quantitatively. Up to now, only indirect methods have been used. These methods, such as fluorescence spectroscopy of labeled monomers,[7,8] chain-end titration by NMR[9−11] or FTIR[12] spectroscopy, or calorimetry,[13] rely on particular association models (isodesmic or cooperative association,[14] ring−chain equilibrium,[15] etc.). The aim of this paper is to show (through a particular example) that the adequate use of a chain stopper (i.e., a monofunctional monomer) can help characterize supramolecular polymers.

Chain stoppers have previously been used to reduce the chain length of supramolecular polymers and thus the viscosity of their solutions[5,16−22] but not to actually block the concentration dependence of the molar mass of supramolecular polymers.

Concept

The concept of the stopper-assisted mass control is illustrated in Figures 1 and 2 with the example of an AB type monomer but can be generalized to any type of structure. As mentioned in the Introduction, the chain length of a supramolecular polymer increases continuously as the concentration is increased (Figures 1a and 2). However, if a chain stopper with a strong association constant is present in a fixed stopper-to-monomer ratio, the chain length increases with the overall concentration only up to a certain concentration C_t, where the

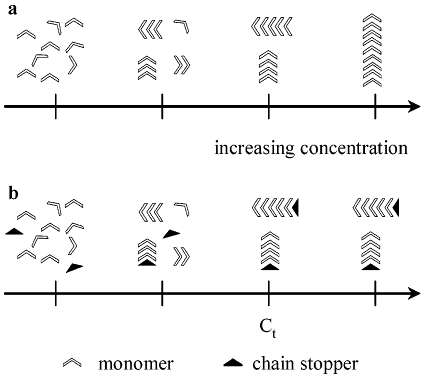

Figure 1. Schematic representation of the influence of concentration on the chain length of a supramolecular polymer without (a) or with (b) a chain stopper at a fixed stopper-to-monomer ratio.

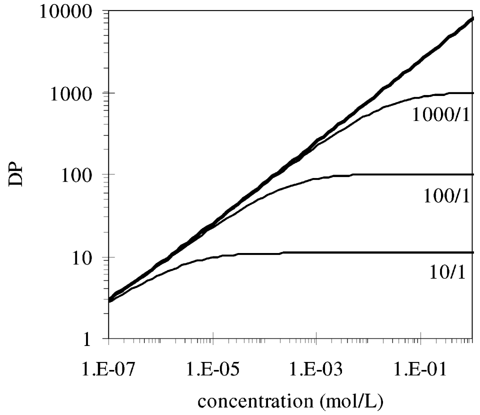

Figure 2. Calculated number-average degree of polymerization for a supramolecular polymer (bold curve) and for 1000/1, 100/1, and 10/1 monomer/chain stopper mixtures (plain curves) vs monomer concentration. The association constant is 6×10^7 L mol^{-1} (see Supporting Information for details).

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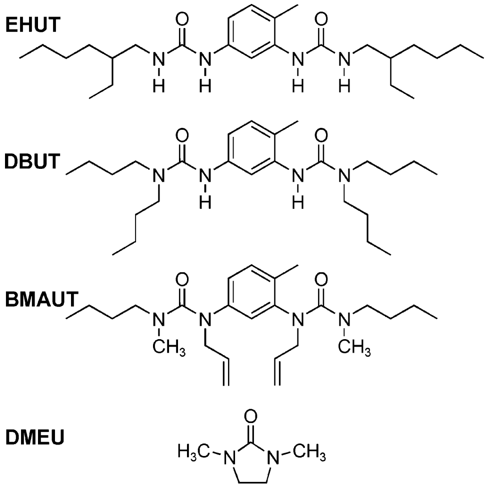
Chart 1. Structures of the Monomer (EHUT) and of the Chain Stoppers (DBUT, BMAUT, DMEU)



vast majority of chains is terminated by a chain stopper (Figures 1b and 2). At concentrations above C_t, the chain length cannot increase further because the stopped chains do not bear any complementary functional group. The difference of behavior between the two cases lies in the fact that for a chain stopped supramolecular polymer there is a minimum number of chains present in solution (i.e., the number of chain stopper molecules) and thus a maximum chain length. On the contrary, for a stopper-free supramolecular polymer, the number of chains present in solution can become vanishingly low when concentration is increased. Consequently, there is a range of concentrations ($C \geq C_\mathrm{t}$) where the molar mass of a supramolecular polymer (with a fixed proportion of chain stopper) is constant. Over this range of concentrations, the physical properties of this system can be considered to vary in the same manner as those of covalent polymers. In particular, scattering or viscosity measurements can be extrapolated to zero concentration (over the range $C \geq C_\mathrm{t}$) to derive characteristic parameters such as the radius of gyration or the second virial coefficient of the chains.

Of course, for this general idea to be of any practical value, the threshold concentration C_t must be sufficiently low, which means that the self-association constant of the monomer (and thus the association constant of the chain stopper) must be large. The remainder of this paper shows through a particular example that it is indeed possible to experimentally apply this concept.

Results and Discussion

The experimental system chosen to test the present concept is the bis-urea-based supramolecular polymer EHUT (Chart 1) in carbon tetrachloride. This compound has been shown to reversibly self-assemble by hydrogen bonding in low-polarity solvents, where it forms long wirelike structures.[12,23]

1. Selection of a Suitable Chain Stopper. Potential chain stoppers have been designed by capping hydrogen bond donor groups on urea or bis-urea (Chart 1). They have been tested by measuring the drop in viscosity of EHUT solutions with an increasing proportion of chain stopper (Figure 3). DBUT is a very efficient chain stopper because only a few percent is sufficient to dramatically reduce the viscosity of EHUT solutions.

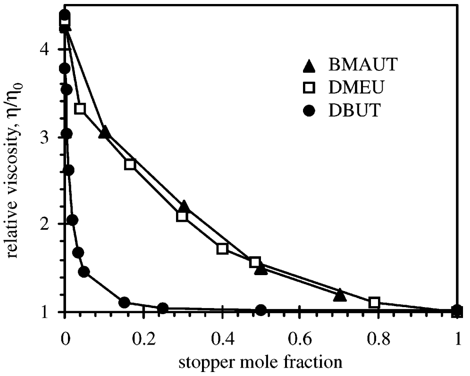


Figure 3. Relative viscosity of mixtures of EHUT and chain stoppers in CCl_4 vs stopper mole fraction. The overall concentration is the same for all experiments ([EHUT] + [stopper] = 3.1 g L^{-1} (7.2 mM for EHUT/DBUT mixtures)).

Mono-urea DMEU is much less efficient, showing that the two urea functions of DBUT interact cooperatively with EHUT, in the same way as EHUT was previously shown to self-assemble cooperatively.[12] Remarkably, BMAUT does not seem to benefit from such a cooperative effect. This is attributed to the fact that the most stable conformations of the urea groups in EHUT and BMAUT are different. Indeed, it has been reported that in the most stable conformation the carbonyl group of a monosubstituted urea is in the cis position relative to the substituent (as depicted in Chart 1). However, the carbonyl group of a N,N-disubstituted urea is more stable in the trans position relative to the aromatic substituent.[24]

DBUT being the most efficient chain stopper, it was selected for the following experiments.

2. Determination of the Relevant Range of Concentrations. By monitoring the presence of free NH groups, infrared spectroscopy is well-suited to quantify the number of chain ends in the present system.[12] Figure 4a shows that a 90/10 EHUT/DBUT mixture at an overall concentration of 2.2 mM is characterized by a small free NH band (3472 cm^{-1}) and a large hydrogen-bonded NH band (3340 cm^{-1}). Interestingly, this spectrum can be matched by adding the spectrum of self-associated EHUT to the spectrum of totally dissociated DBUT (Figure 4b). This fact yields no information about the interaction between DBUT and EHUT because, obviously, the same spectrum would be expected if no interactions were present. However, it means that for the 90/10 EHUT/DBUT mixture at a concentration of 2.2 mM the number of unstopped chains is negligible compared to the number of chain stoppers (whether the latter are attached to a chain end or free). Moreover, if we assume that the association constant of DBUT with EHUT is at least of the same order of magnitude as that of the self-association of EHUT (as indicated by the viscosity measurements), then the concentration of free DBUT can be neglected. Consequently, the concentration at which the vast majority of chains are terminated by a chain stopper (C_t) is lower than 2.2 mM. The results for the same experiment, repeated over a large range of concentrations, are summarized in Figure 5. At low concentrations (between 0.2 and 15 mM), the ratio of the free NH band to the hydrogen-bonded NH band is constant. It means first that $C_\mathrm{t} < 0.2$ mM because at concentrations lower than C_t this ratio should increase due to the presence of unstopped chains. Additionally, it confirms that DBUT interacts with EHUT through

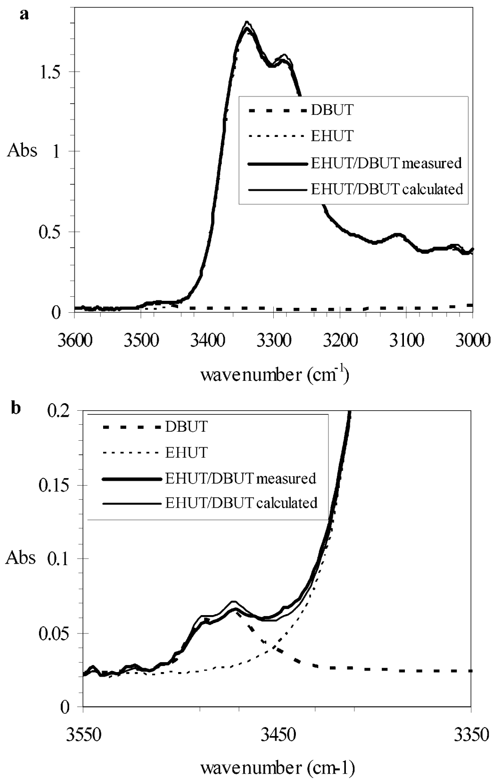


Figure 4. FTIR spectra of solutions in CCl_4 (complete NH region (a) and magnification of the free NH region (b)). EHUT: EHUT at 2.0×10^{-3} mol L^{-1}; DBUT: DBUT at 2.2×10^{-4} mol L^{-1}; EHUT/DBUT experimental: EHUT at 2.0×10^{-3} mol L^{-1} with DBUT at 2.2×10^{-4} mol L^{-1}; EHUT/DBUT calculated: summation of EHUT and DBUT.

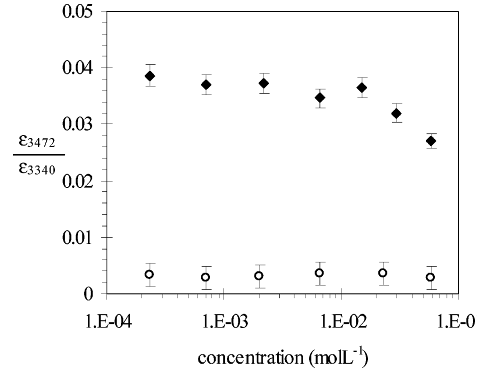


Figure 5. Ratio of absorbances measured at 3472 cm^{-1} (free) and 3340 cm^{-1} (hydrogen bonded) vs concentration for EHUT solutions (○) and 90/10 EHUT/DBUT mixtures (◆) in CCl_4.

the carbonyl groups and not through the NH groups because the DBUT NH groups are not hydrogen bonded and we know from Figure 3 that DBUT is an efficient chain stopper in this concentration range.[25] Furthermore, Figure 5 shows that at concentrations higher than 15 mM the free to hydrogen-bonded NH ratio decreases, revealing that the NH functions of the chain stopper DBUT can also participate in hydrogen bonding. The butyl substituents are apparently not bulky enough to completely avoid this additional interaction, making DBUT unreliable as a chain stopper at concentrations higher than 15 mM.

Consequently, the concentration dependence of the molar mass of 90/10 EHUT/DBUT mixtures can be considered to be effectively blocked over the range of concentrations from 0.2 mM (or lower) to 15 mM.[26]

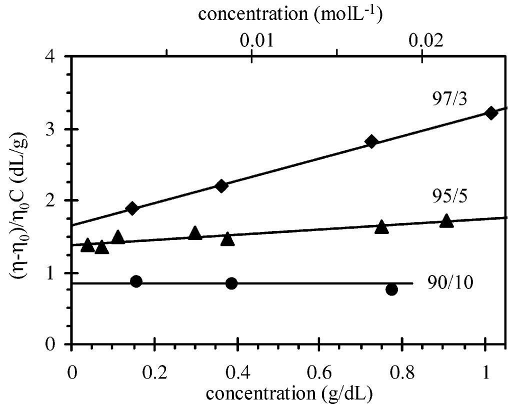


Figure 6. Reduced specific viscosity of 97/3, 95/5, and 90/10 EHUT/DBUT mixtures vs overall concentration in CCl_4.

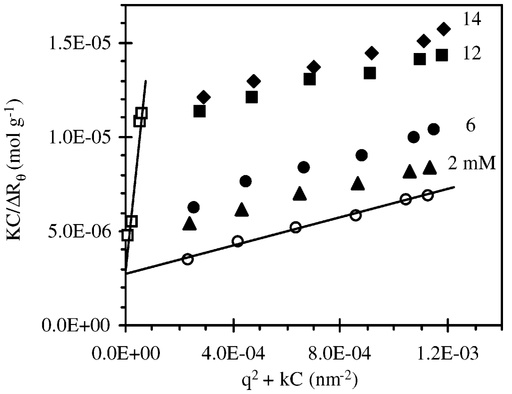


Figure 7. Static light scattering data (Zimm plot) for 99.5/0.5 EHUT/DBUT mixtures in CCl_4 ($k = 0.01$ cm^3 g^{-1} nm^{-2}).

3. Characterization of Stopped Chains. Figure 6 shows that EHUT/DBUT mixtures yield linear plots in the reduced specific viscosity representation classically used in polymer science. The intrinsic viscosity for these mixtures can be deduced by extrapolation to zero concentration and is reported in Table SI1 (Supporting Information). The intrinsic viscosity decreases when the chain stopper content increases, in agreement with the expected shortening of the supramolecular chains.

Static light scattering is used in polymer science to measure the weight-average molar mass by extrapolation to zero of both concentration and measuring angle. Figure 7 shows the classical Zimm representation used for this double extrapolation in the case of 99.5/0.5 EHUT/DBUT mixtures. As in the case of nonaggregating covalent polymers, the plots are linear. Although the linearity of these data (light scattering and viscosity) does not prove in itself that the molar mass of the chains is constant, a nonlinearity of the plot would be a clear sign of molar mass evolution with concentration. The characteristic information that can be derived from the Zimm plot (weight-average molar mass (M_w), radius of gyration (R_g), and second virial coefficient (A_2)) are reported in Table 1. The values of M_w and R_g decrease significantly when the chain stopper content increases, again in agreement with the expected shortening of the supramolecular chains. The value of A_2 seems to be unaffected by this shortening and can thus be considered to be a characteristic of the structure of EHUT chains in this solvent. More quantitatively, the measured values of M_w can be compared to the expected value for the number-average molar mass (M_n in Table 1), calculated by assuming that each supramolecular

Table 1. Parameters Deduced from Light Scattering Data for Mixtures of EHUT and DBUT in CCl_4

EHUT/DBUT^a	$M_{n,calc}$^{b}	M_w^{c}	R_g^{d}	A_2^{e}	R_h^{f}
90/10	4.3	57	24	8.0	9
97/3	14.4	173	43	8.8	16
99.5/0.5	86.5	830	63	7.1	51

^{a} Molar ratio of the 2 compounds. ^{b} Calculated number-average molar mass, assuming that each supramolecular chain contains one chain stopper, in kg mol^{-1}. ^{c} Measured weight-average molar mass, in kg mol^{-1}. ^{d} Radius of gyration, in nm. ^{e} Second virial coefficient, in 10^{-4} mol g^{-2} cm^3. ^{f} Hydrodynamic radius, in nm.

chain contains one chain stopper. The ratio between measured M_w and expected M_n lies between 9 and 13. These large values can result from two nonexclusive effects. First, it is likely that the polydispersity of these systems is larger than 2 due to the nonisodesmic nature of the self-association of EHUT. Indeed, it has been shown that the polydispersity of EHUT supramolecular polymers in chloroform can be as high as 6.[12] Second, we cannot exclude that several chain stopper molecules are necessary to effectively stop one supramolecular chain.

Dynamic light scattering performed on the same solutions reveals that the distributions of relaxation times derived from the correlation functions are characterized by a single relaxation process. In all cases, the characteristic average relaxation times (τ) are q^2-dependent (where q is the scattering wave vector), meaning that diffusive motions are probed. They can thus be used to calculate apparent diffusion coefficients $D = (q^2\tau)^{-1}$. The plot of the apparent diffusion coefficient vs concentration is linear (Figure SI1) and affords the diffusion coefficient (D_0) by extrapolation to zero concentration. Finally, the hydrodynamic radius of the scattering species has been estimated using the Stokes–Einstein relation $R_h = kT/6\pi\eta D_0$, where k is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent (Table 1). The high values of the ratio R_g/R_h are in agreement with the highly anisotropic shape previously deduced from SANS measurements.[23b]

4. Molar Mass Measurements in Stopper-Free Solutions. The information deduced from these experiments with a chain stopper can then be used to characterize stopper-free solutions. For example, the determination of the second virial coefficient (A_2) makes it possible to correct finite concentration effects in pure EHUT solutions, if the concentration dependence of A_2 is negligible, which seems to be the case here (Table 1). Accordingly, M_w and R_g have been determined for several EHUT concentrations (C), from the angle dependence of the Rayleigh ratio (ΔR_θ), through eq 1.

$$\frac{KC}{\Delta R_\theta} - 2A_2C = \frac{1}{M_w}\left(1 + \frac{q^2{R_g}^2}{3}\right) \qquad (1)$$

Figure 8 shows the results for concentrations below the overlap concentration, which can be estimated to be on the order of 0.01 mol L^{-1} (see Figure 1 from ref 12).

To test the validity of this approach, it is possible to compare the M_w data to results obtained independently from calorimetric measurements (ITC). The principle of the technique is to measure the heat evolved while aliquots of a relatively concentrated EHUT solution are injected into pure solvent (placed in a calorimetric cell at a fixed temperature). The recently described[13] ITC procedure to determine the association constants of supramolecular polymers was applied to EHUT in CCl_4. The detailed results are provided as Supporting Information. From the association constants, the evolution of M_w with concentration was calculated (Figure 8). The close agreement between light scattering and calorimetric data is particularly remarkable, as no fitting parameter is involved.

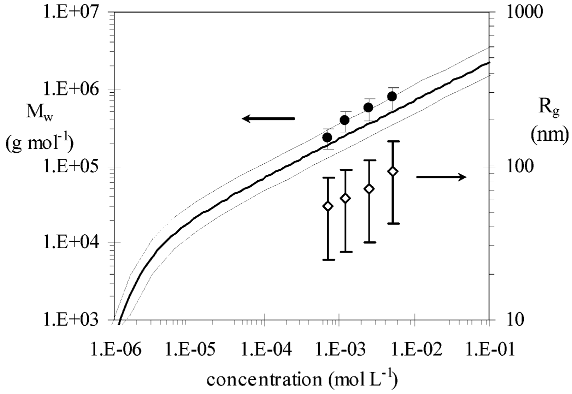


Figure 8. Determination by static light scattering (●) and calorimetry (full curve) of the weight-average molar mass for EHUT vs concentration in CCl_4, at 25 °C. The dotted curves represent the uncertainty of the calorimetric data. R_g (◇) is determined by static light scattering.

Conclusion

The present experimental results show that an efficient chain stopper can actually block the concentration dependence of the molar mass of supramolecular polymers over a realistic concentration range. This property can be used to characterize the stopped supramolecular chains by classical polymer characterization techniques (viscosimetry, light scattering, etc.). This in turn makes it possible to derive some information about the supramolecular polymer in the absence of a chain stopper.

Experimental Section

Synthesis. The synthesis of EHUT and BMAUT was previously reported.[23b]

1,1-Dibutyl-3-[3-(3,3-dibutylureido)-4-methylphenyl]-urea (DBUT). To a stirred solution of 2,4-toluene diisocyanate (Fluka, 99%, 3.4 mL, 23 mmol) in dichloromethane (125 mL, distilled over phosphorus pentoxide), dibutylamine (Aldrich, 6.4 g, 50 mmol) in dichloromethane (75 mL) was added under nitrogen. After 24 h, the solvent was evaporated, and purification was performed by silica gel column chromatography with dichloromethane/ethyl acetate (88/12) as the eluent. Recrystallization in heptane afforded 6.9 g of a white solid (69%); mp 111 °C. ^{1}H NMR (300 MHz, D_6-DMSO): δ (ppm) = 8.02/7.61 (2s, 2H, Ar−N*H*), δ = 7.33 (s, 1H, Ar−*H*), δ = 7. 17/6.98 (2d, J = 9.4 Hz, 2H, Ar−*H*), δ = 3.25 (m, 8H, N−CH_2), δ = 2.06 (s, 3H, Ar−CH_3), δ = 1.48/1.28 (m, 16H, CH_2), δ = 0.90 (t, J = 7.1 Hz, 12H, CH_3). ^{13}C NMR (75 MHz, D_6-DMSO): δ (ppm) = 155.6/155.2 (*C*=O), δ = 138.4/137.9/129.2/126.3/118.1/116.4 (*Ar*), δ = 46.0/45.9 (N−CH_2), δ = 30.4/19.5/17.2 (CH_2), δ = 13.8/13.7 (CH_3). Anal. Calcd for $C_{25}H_{44}N_4O_2$: C, 69.40; H, 10.25; N, 12.95; O, 7.40. Found: C, 68.86; H, 10.30; N, 12.85; O, 7.99.

Characterizations. Carbon tetrachloride was used as received. Solutions were prepared at least 1 day prior to the measurements.

Viscometry. Solutions were filtered through Millex filters (porosity 0.45 μm). Measurements were performed at 25 ± 0.1 °C with a Cannon-Manning semi-microcapillary viscometer.

IR Spectroscopy. Infrared spectra were recorded at room temperature on a Nicolet Avatar 320 spectrometer in KBr cells of 0.05−2.5 cm path length.

Light Scattering. Static and dynamic light scattering measurements were performed with an experimental setup previously described,[27] at a wavelength (λ_0) of 514.5 nm and a temperature of 25 °C. Solutions were filtered through Whatman Anotop filters (porosity 0.2 μm). The specific refractive index increment for EHUT in CCl_4 has been measured by differential refractometry ($dn/dC = 0.0756$ mL/g).

Supporting Information Available: Viscosimetric, scattering, and calorimetric data. This material is available free of charge via the Internet at http://pubs.acs.org.

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